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(54) Aqueous dispersions of fluorinated polyurethanes

(57) Process for protecting wood, marble, stones, bricks, plaster, cement and similar materials, used in particular in building, from the degradation caused by atmospheric and polluting agents, by applying on the surface of said materials a protective agent selected from aqueous dispersions of fluorinated polyurethanes, the fluorinated part deriving from fluoropolyether units, having high number average molecular weight, at least 9000, and having a fluorine content higher than 25% by weight and containing in their structure hydrophilic ionic groups of cationic or anionic nature, wherein the cationic or anionic groups are present as side groups with respect to the polyurethane polymeric chain.

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Description

The present invention relates to a process for protecting wood, marble, stones, bricks, plaster, cement and similar materials from the action of atmospheric and polluting agents.

In particular the process relates to the application of a coating endowed with superior oil- and water-repellence combined with high durability.

It is known the use of perfluoropolyethers for surface applications on the above mentioned materials conferring high hydrophobic and oleophobic properties to the surface of the treated materials. See for instance European patent No. 59100.

The perfluoropolyethers utilized in the aforesaid patent had inert end groups, namely perfluoroalkyl radicals.

The drawback of these products is that the presence of porosity in the material to be protected leads to phenomena of slow absorption, thus the protection effectiveness decreases in time. Moreover these products tend to be washed away by atmospheric agents.

It was needed, therefore, the use of additional treatments to protect surfaces, even though the part migrating inside had a barrier effect which reduced the amount of product to be utilized for subsequent treatments.

To ovecome this drawback, it is known in the art the use of functionalized perfluoropolyethers, i.e. having end-groups capable of fixing to the substrate to be protected, thus reducing the perfluoropolyether mobility and increasing the protection durability of the treated product. See for instance EP Patents 215,492 and 192,493.

Even though durability is improved with respect to the perfluoropolyethers with neutral end-groups of the patent above, it has been noticed that, depending on the material porosity, also these products do not give optimum durability, therefore also in this case subsequent superficial treatments are necessary.

It is also known the use of dispersions or aqueous emulsions of fluorinated polyurethanes for treating the above mentioned materials. See for instance European patent application 92115930.7. The results obtained as initial protection are similar.

It has now been surprisingly and unexpectedly found that it is possible to increase initial effectiveness of the protective treatment as to oil and water-repellence combined with a high durability of the superficial treatments on the above mentioned materials, and in particular on wood and cement, if the products of the present invention described hereinafter are utilized.

Object of the present invention is therefore a process for protecting wood, marble, stones, bricks, plaster, cement and similar materials used in particular in building, from the degradation caused by atmospheric and polluting agents, by applying on the surface of said materials a protective agent selected from aqueous dispersions of fluorinated polyurethanes, the fluorinated part deriving from fluoropolyether units, having high number average molecular weight, at least 9000, and having a fluorine content higher than 25% by weight, and containing in their structure hydrophilic ionic groups of cationic or anionic nature, wherein the cationic or anionic groups are present as side groups with respect to the polyurethane polymeric chain, being separated from the latter by a bivalent alkylene radical $(R)_a$ selected from CR_1R_2 and $Y(CR_1R_2)_b$ wherein:

Y is a linking bivalent radical different from CR_1R_2, for instance COO, CONH, OCONH, O; b is an integer from 0 to 20;

R_1 and R_2, equal or different from each other, are H, aliphatic radicals having from 1 to 10 carbon atoms, cycloaliphatic radicals having from 5 to 20 carbon atoms, aromatic radicals having from 6 to 20 carbon atoms, the cyclic radicals containing optionally heteroatoms;

a being an integer from 1 to 20, preferably from 3 to 10.

The present invention is based on the unexpected fact that with the polyurethanes of the present invention it is possible to obtain an increase as to oil- and water-repellence combined with an increase of the durability of the superficial treatment and therefore a maintenance of oil- and water-repellence in time with respect to the known and exemplified products mentioned above.

The preparation of fluorinated polyurethanes having high molecular weight and high fluorine content is described for instance in USP 4,983,666 and in European patent application 92115930.7, but using hydrophilic ionic groups present as side groups of the main polymeric chain as defined above.

In practice the polyurethanes of the invention are obtained by a two-stage polymerization according to various known processes which have in common the 1st step wherein a fluorinated diisocyanate prepolymer is prepared in a polar organic solvent, for instance ketones and acetates, and a 2nd step which, depending on the process, consists in:

I) partial chain-extension with traditional chain-extenders, such as low molecular weight diols or diamines, well known in the art cited above, incorporated herein by reference, and ionomers, as according to the present invention; then subsequent dispersion in water and salification with polymerization completion by formation of ureidic bonds;

or

II) introduction of ionomers and then dispersion, salification and polymerization by chain-extension in water with diamines;

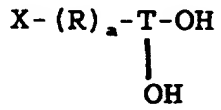
or

III) introduction of ionomers and completion of the chain-extension in solvent, to obtain the polymer with the desired molecular weight, and then subsequent dispersion and salification in water of the so obtained polymer.

In the 1st step the diisocyanate fluorinated prepolymer is prepared according to known techniques, for instance by reaction of a (per)fluoropolyether (PFPE) having alcohol or acid end-groups with hydrogenated diisocyanates.

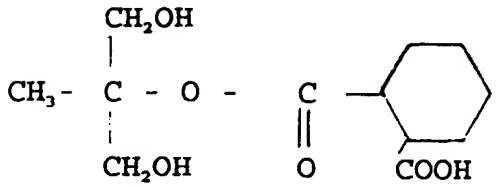
The PFPE with said end-groups can optionally be mixed with hydrogenated macrodiols, for instance PTMEG (polytetramethylenglycol), PCL (polycaprolactonediol), PEG (polyethyleneglycol), PPG (polypropylenglycol), PBDH (polybutadiendiol).

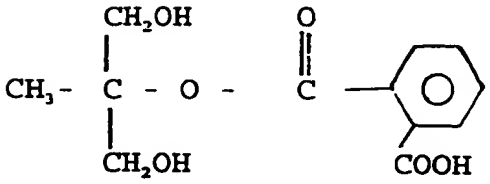
The ionomers utilizable according to the present invention correspond for instance to the formula:

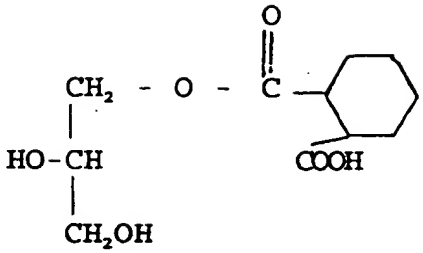


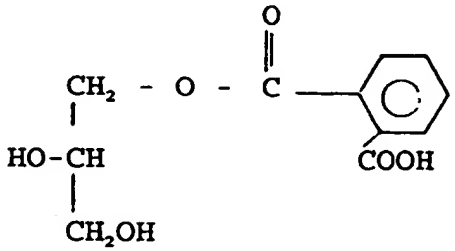
wherein T is an alkylene radical from 1 to 20 C atoms and has the meaning of R_1, X = $N(R_1)_2$, COOH, SO_3H.

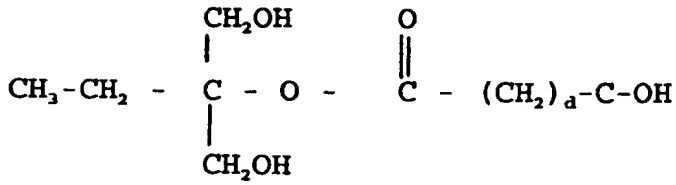
As diol structures containing carboxylic groups, the following can be cited:





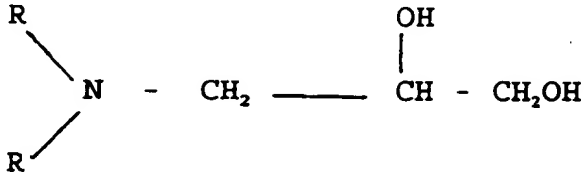




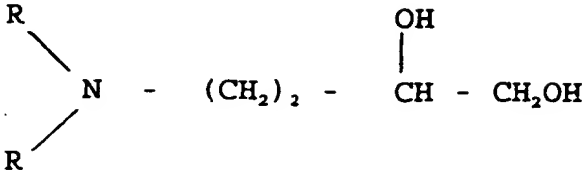


d = 2-3.

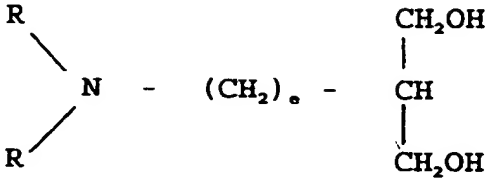
As diol structures containing substituted amino groups, for instance the following can be cited:



wherein R has the meaning indicated above for R_1,

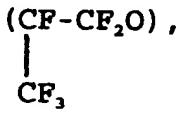


wherein R has the meaning indicated above for R_1,

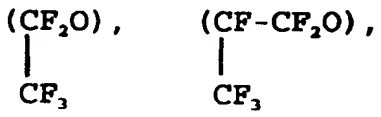


e = 1-10.

PFPE to be utilized in the 1st step are, for instance, those having an average molecular weight of from 500 to 3000 and preferably from 1000 to 2000, and containing repetitive units selected from the following:



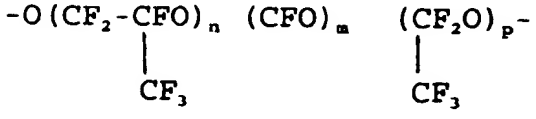
(CF_2CF_2O),



$(CF_2CF_2CF_2O)$, $(CF_2CF_2CH_2O)$, said units being statistically distributed in the PFPE polymeric chain.

In particular they belong to one or more of the following classes:

1)



having "random" distribution of perfluorooxyalkylene units, and n, m, p have mean values such as to meet the aforesaid requirements of average molecular weight;

2) $-O(CF_2CF_2O)_{n'}(CFO)_{m'}-$ - with random distribution of the perfluorooxyalkylene units, m' and n' are integers such as to meet the aforesaid requirements;

3) $-O(CF_2CF_2O)_{n''}(CF_2O)_{m''}-$

$$-(CFO)_{p''}- \qquad -(CF-CF_2O)_{o''}-$$
$$\quad | \qquad\qquad\quad |$$
$$\quad CF \qquad\qquad CF_3$$

m", n", p", o" are integers such as to meet the requirements indicated above;

4)

$$-O(CF_2-CFO)_t-$$
$$\qquad\quad |$$
$$\qquad CF_3$$

t is an integer such as to meet the aforesaid requirements;

5) $-O(CF_2CF_2O)_z$

z is an integer such as to meet the aforesaid requirements;

6) $-O(CF_2CF_2CF_2O)_s-$ or $-O(CF_2CF_2CH_2O)-$

s in an integer such as to meet the aforesaid requirements.

The fluorinated polyurethane has high molecular weight, generally from 10000 to 50000, preferably 20000-30000; the F content is preferably from 30 to 40% by weight.

Some working examples of the present invention are reported hereinafter, the purpose of which is only illustrative but not limitative of the scope of the invention itself.

Preparation of fluorinated polyurethanes

EXAMPLE 1A - Fluorinated anionic polyurethane (comparative)

A fluoropolyoxyalkylene diol (Fluorolink(R) D) having a hydroxy equivalent weight of 1020 g/equivalent was slowly charged into a flask containing 22.23 g of isophoron diisocyanate (molecular weight = 222.29 g/mole) and 2 drops of dibutyl tin dilaurate in 4 hours.

An opaque immiscible mixture was obtained. After stirring for further two hours, the reaction mixture became clear and the viscosity increased. 50 g of N-methyl pyrrolidone were added to this reactive mixture, together with 6.71 g of 2,2-bis(hydroxymethyl) propionic acid. Non-miscibility was noticed again. The reaction temperature was increased to 80°C and kept for 8 hours for producing a clear product having high viscosity. 50 additional g of N-methyl pyrrolidone were loaded to dilute the solution. The reaction temperature was lowered to 60°C and 3.0 g of a solution of concentrated ammonia (content in ammonia of 28%) were loaded. After homogeneously mixing, deionized water was loaded to give an aqueous dispersion/solution with a resin content of 23% by weight.

EXAMPLE 2 - Fluorinated cationic polyurethane

A fluoropolyoxyalkylene diol (Fluorolink(R) D) having an hydroxy equivalent weight of 1020 g/equivalent was slowly loaded in a flask containing 22.23 g of isophoron diisocyanate (molecular weight = 222.29 g/mole) and 2 drops of dibutyl tin dilaurate for over 4 hours.

After stirring for futher two hours the reaction mixture became transparent and the viscosity increased. 50 g of N-methyl pyrrolidone were added to this reaction mixture, together with 5.96 g of 3-(dimethylamino)-1,2-propandiol. Non-miscibility was noticed. The reaction temperature was increased to 80°C and kept for 8 hours to produce a transparent product having high viscosity. 50 additional g of N-methyl pyrrolidone were loaded to dilute the solution. The reaction temperature was lowered to 60°C and 3.0 g of acetic acid were charged. After homogeneously mixing, deionized water was loaded to give an aqueous dispersion/solution with a resin content of 22% by weight.

EXAMPLE 2A

Example 2 was repeated using however as tertiary amine N-methyldiethanolamine having formula $CH_3N(CH_2CH_2OH)_2$ in equimolar amount.

An aqueous dispersion/solution having 27% by weight of resin was obtained.

APPLICATIVE EXAMPLES

Application of fluorinated polyurethanes as protective agents for imparting water- and oil-repellence properties to wood and building materials. Methods utilized for the characterization:

Test No. 1 Water-repellence evaluation

The resistance of the surface to be wet by water/alcohol solutions is measured, classifying the water-repellence with a number corresponding to the composition of solutions having different water/isopropanol ratio. A drop is deposited on the surface and if after 10 seconds no absorption is noticed, the subsequent classification number is evaluated.

WATER-REPELLENCE (WR)

Class	Composition
W	water
1	90/10 water/isopropanol
2	80/20 water/isopropanol
3	70/30 water/isopropanol
4	60/40 water/isopropanol
5	50/50 water/isopropanol
6	40/60 water/isopropanol
7	30/70 water/isopropanol
8	20/80 water/isopropanol
9	10/90 water/isopropanol
10	isopropanol

A higher number indicates a greater water-repellence.

A value of at least 4 or 5 as water-repellence is condidered satisfactory.

Test No. 2 Oil-repellence evaluation

The resistance of the surface to be wet by oils is measured, classifying the oil-repellence with a number corresponding to hydrocarbons having different surface tension. A drop is deposited on the surface and if after 30 seconds no absorption is noticed, the subsequent classification number is evaluated.

OIL-REPELLENCE (OR)

Class	Oil	Dyne/cm
1	Vaseline oil	31.5
2	Vaseline/n-hexadecane (65/35)	29.5
3	hexadecane	27.3
4	n-tetradecane	26.4
5	n-dodecane	24.7
6	n-decane	23.5
7	n-octane	21.4
8	n-heptane	19.8.

A higher number indicates a greater oil-repellence.
A value of at least 4 as oil-repellence is condidered satisfactory.

Test No. 3 - Water and oil-repellence evaluation for prolonged contact times

The test evaluates the time necessary for a water drop and a hexadecane drop to be absorbed by the treated substrate in comparison with the untreated surface.

Test No. 4 - Water and oil-repellence evaluation after surface washing

The test evaluates with the methods described for test Nos. 1 and 2 the water- and oil-repellence of a surface after prolonged washing. An artificial rain is simulated submitting the test pieces to a water jet (capacity: about 4 liters/minute) for 30 minutes.

The maintenance of water- and oil-repellence or at most the variation of a class is desirable.

EXAMPLE 3

Water- and oil-repellence application test of the product of Example 2 applied on asbestos cement (Cembonit$^{(R)}$ of Società Italiana Lastre having 1.4 Kg/dm^3 density.

The aqueous composition of the cationic fluorinated polyurethane (PU) obtained according to the method of Example 2 was diluted to 5% by weight with water and utilized for brush treating of small asbestos cement plates. Amounts corresponding to about 5 and 10 g of polymer/m^2 were deposited.

After drying for 48 hours at room temperature, the water- and oil-repellence was evaluated according to test Nos. 1 and 2. The obtained results are reported in Table 1.

EXAMPLE 4

Water- and oil-repellence application test of the product of Example 2 applied on asbestos cement (of Example 3)

The aqueous composition of the cationic fluorinated polyurethane (PU) obtained according to the method of Example 2A was diluted to 5% by weight with water and utilized for brush treating of asbestos cement plates. Amounts corresponding to about 5 and 10 g of polymer/m^2 were deposited.

After drying for 48 hours at room temperature the water- and oil-repellence was evaluated according to test Nos. 1 and 2. The obtained results are reported in Table 1.

TABLE 1

Sample	g/m²	WR	OR
PU Example 2	0	immediate abs.	immediate abs.
	4	4	5
	9	5	6
PU Example 2A	5	2	5
	12	3	6

EXAMPLE 5

Water- and oil-repellence application test with prolonged contact times with water and hexadecane of the products of Example 2 and 2A applied on asbestos cement

The water- and oil-repellence given from the samples of fluorinated polyurethane, obtained according to the method described in examples 2 and 2A, to asbestos cement surfaces were evaluated according to test No. 3 after drying of 48 hours at room temperature. The polyurethanes were applied in the form of aqueous systems diluted to 5% by weight as described in examples 3 and 4. The experimental data (Table 2) report the time at which initial absorption or penetration of water and hexadecane in the substrates is detected

TABLE 2

Sample	g/m²	water abs.	hexadecane abs.
PU Example 2	0	immediate	immediate
	4	45 minutes	30 minutes
	9	2 hours	2 hours
PU Example 2A	5	15 minutes	15 minutes
	12	20 minutes	20 minutes.

The data reported in Table 2 qualitatively confirm the results of Table 1 and show that the fluorinated polyurethane whose preparation is described in example 2 has a better water-repellence compared with the fluorinated polyurethane whose preparation is described in example 2A. The best oil-repellence of the sample relating to example 2 is maintained also with prolonged contact times with hexadecane.

EXAMPLE 6

Water- and oil-repellence application test with prolonged contact times with water and hexadecane of the products of Examples 2 and 2A applied on wood.

The aqueous compositions of the cationic fluorinated polyurethane (PU) obtained according to the method of Example 2 and 2A were diluted to 5% by weight with water and utilized for brush treating of pinewood plates. Amounts corresponding to about 5 and 10 g of polymer/m² were deposited.

After drying for 48 hours at room temperature the water- and oil-repellence was evaluated according to test No. 3. The obtained results are reported in Table 3.

TABLE 3

Sample	g/m²	water abs.	hexadecane abs.
PU Example 2	0	3 minutes	immediate
	5	3 hours	30 minutes
	9	3 hours	30 minutes
PU Example 2A	7	1 hour	20 minutes
	9	1 hour	30 minutes.

EXAMPLE 7

Water- and oil-repellence application test of the products of Examples 2 and 2A and of comparative products applied on wood.

The aqueous compositions of the cationic fluorinated polyurethane (PU) obtained according to the method of Example 2 and 2A were diluted to 5% by weight with water and utilized for brush treating of oak-veneered wood plates.

As comparison (Ex. 7A) the same type of substrate was treated with an aqueous solution at 2% by weight of a perfluoropolyether product having the structure of formula 1 with number average molecular weight 700, monofunctional with $COO^-NH_4^+$ end-groups, the other end-group being preferably a perfluoroalkyl; and (Ex. 7B) with a 5% by weight solution in Algofrene(R) 113 of a fluoropolyether having $-CH_2OH$ end-groups (Fluorolink(R) D) having number molecular weight 1000 (equivalent weight 540).

Amounts corresponding to about 5 and 10 g of polymer/m² were deposited.

After drying for 48 hours at room temperature, the water- and oil-repellence was evaluated according to test Nos 1 and 2. The results are reported in Table 4.

TABLE 4

Sample	g/m²	WR	OR
PU Example 2	0	W	2
	5	5	5
	9	6	6
PU Example 2A	4.5	3	4
	10	4	5
Product Ex. 7B	5	2	3
	11	3	4
Product Ex. 7A	5	W	3
	8	W	3.

EXAMPLE 8

Water- and oil-repellence application test after washing the products of Examples 2 and 2A and comparative products applied on wood.

The wood plates treated as shown in Example 7 are submitted to a prolonged washing as described in test No. 4. After drying for 3 days at room temperature the water-repellence according to test No. 1 was evaluated, obtaining the

results described in Table 5.

TABLE 5

Sample	g/m²	WR
PU Example 2	0	W
	5	4
	9	4
PU Example 2A	4.5	2
	10	3
Product Ex. 7B	5	W
	11	W.

Claims

1. Process for protecting wood, marble, stones, bricks, plaster, cement and similar materials used in particular in building, from degradation caused by atmospheric and polluting agents, which comprises applying on the surface of said materials a protective agent selected from aqueous dispersions of fluorinated polyurethanes, the fluorinated part deriving from fluoropolyether units, having high number average molecular weight and a fluorine content higher than 25% by weight and containing in their structure hydrophilic ionic groups of cationic or anionic nature, wherein the cationic or anionic groups are present as side groups with respect to the polyurethane polymeric chain, being separated from the latter by a bivalent alkylene radical $(R)_a$ selected from CR_1R_2, and $Y(CR_1R_2)_b$
wherein:
Y is a linking bivalent radical different from CR_1R_2, for instance COO, CONH, OCONH, O; b is an integer from 0 to 20, R_1 and R_2 equal or different from each other are H, aliphatic radicals having from 1 to 10 carbon atoms, cycloaliphatic radicals having from 5 to 20 carbon atoms, aromatic radicals having from 6 to 20 carbon atoms, the cyclic radicals containing optionally heteroatoms;
a being an integer comprised from 1 to 20.

2. Process according to claim 1, wherein the polyurethane fluorinated part comprises perfluorooxyalkylene units.

3. Process according to claims 1 and 2, wherein the fluorooxyalkylene units have average molecular weight comprised from 500 to 3000 and containing repetitive units selected from:

$$(CF(CF_3)-CF_2O),$$

(CF_2CF_2O),

$$(CF_2O), \qquad (CF(CF_3)-CF_2O),$$

$(CF_2CF_2CF_2O)$, $(CF_2CF_2CH_2O)$, said units being statistically distributed along the polymeric chain.

4. Process according to claim 3, wherein the fluorooxyalkylene units are
$-(OCF_2CF_2O)_{n'}(CFO)_{m'}-$
with random distribution of perfluorooxyalkylene units, m' and n' are integers such as to meet the aforesaid requirements.

5. Process according to claims from 1 to 4, wherein the molecular weight of the fluorinated polyurethane ranges from 20000 to 30000, the fluorine content being comprised between 30% and 40% by weight.

6. Process for preparing polyurethanes of claims 1-5 by a two-step polymerization wherein in the 1st step a fluorinated diisocyanate prepolymer is prepared in an organic solvent and the 2nd step consists in:

I) partial chain-extension with traditional chain-extenders, such as low molecular weight diols or diamines, and ionomers containing the bivalent alkylene radical $(R)_a$; then subsequent dispersion in water and salification with polymerization completion by formation of ureidic bonds;

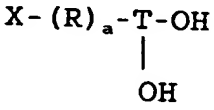
or

II) introduction of ionomers as defined in point I) and then dispersion, salification and polymerization by chain-extension in water with diamines;

or

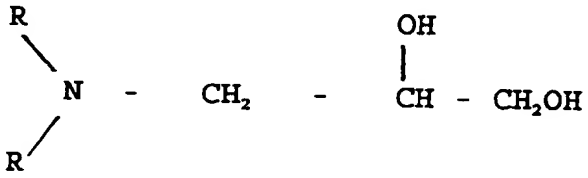
III) introduction of ionomers as defined in point I) and completion of the chain-extension in solvent, to obtain the polymer with the desired molecular weight, and then subsequent dispersion and salification in water of the so obtained polymer.

7. Process according to claim 6, wherein the ionomers utilizable according to the present invention have formula:



wherein T is an alkylene radical from 1 to 20 C atoms and has the meaning of R_1, X = $N(R_1)_2$, COOH, SO_3H.

8. Process according to claim 7, wherein the chain extender has formula:



wherein the R groups have the same meaning of R_1.

9. Fluorinated polyurethanes wherein the fluorinated part is derived from fluoropolyether units, having number average molecular weight of at least 9000, and having a fluorine content higher than 25% by weight and containing in their structure hydrophilic ionic groups of cationic or anionic nature wherein the cationic or anionic groups are present as side groups with respect to the polyurethane polymeric chain, being separated from the latter by a bivalent alkylenic radical $(R)_a$ selected from CR_1R_2 and $Y(CR_1R_2)_b$
wherein:
Y is a linking bivalent radical different from CR_1R_2, for instance COO, CONH, OCONH, O;
b is an integer from 0 to 20; R_1 and R_2, equal or different from each other, are H, aliphatic radicals having from 1 to 10 carbon atoms, cycloaliphatic radicals having from 5 to 20 carbon atoms, aromatic radicals having from 6 to 20 carbon atoms, cyclic radicals optionally containing heteroatoms;
a being an integer comprised between 1 and 20.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 10 8724

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	EP-A-0 533 159 (SYREMONT) * page 2, line 42 - page 5, line 18 *	1-9	B27K3/15 C04B41/48 C08G18/50 C08G18/08
A	EP-A-0 337 312 (AUSIMONT) * page 2, line 30 - page 4, line 44 *	1-9	
A	EP-A-0 430 266 (SYREMONT) * page 3, line 1 - page 5, line 27 *	1-9	
A	EP-A-0 273 449 (AUSIMONT) * page 3, line 5 - page 5, line 56 *	1-9	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B27K
C04B
C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	6 October 1995	Schmidt, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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